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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US89/04011 (22) International Filing Date: 15 September 1989 (15.09.89) (30) Priority data: 247,026 20 September 1988 (20.09.88) US (71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025 (US). (72) Inventors: SHAFE, Jeff ; 3323 Spring Street, Redwood City, CA 94053 (US). STRALEY, O., James ; 770 9th Avenue, Redwood City, CA 94063 (US). OSWAL, Ravinder, K. ; 4832 La Habra Street, Union City, CA 94587 (US). McCARTY, Gordon ; 2244 Belthorn Court, San Jose, CA 95131 (US). DHARIA, Amitkumar, N. ; 5699 Civic Terrace Avenue, Newark, CA 94560 (US).		(74) Agents: BURKARD, Herbert, G. et al.; Raychem Corporation, 300 Constitution Drive, Menlo Park, CA 94025 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: CONDUCTIVE POLYMER COMPOSITION (57) Abstract A polymer thick film ink which exhibits PTC behavior comprising an organic polymer which is crystalline, an active solvent suitable for dissolving the polymer, and carbon black which has a pH of less than 4.0. The ink is particularly useful in producing electrical devices such as heaters and circuit protection devices.		

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CONDUCTIVE POLYMER COMPOSITION

BACKGROUND OF THE INVENTIONField of the Invention

This invention relates to conductive polymer compositions for use as polymer thick film inks and methods of making said inks.

Background of the Invention

Thick film inks for use as resistors, connectors and other electrical components are known. These conventional inks normally exhibit ZTC behavior (zero temperature coefficient of resistance), i.e. they maintain a relatively constant resistance value over a temperature range of interest. The inks are usually applied via screen-printing or other means to a rigid substrate, e.g. alumina, beryllia, or glass; the rigid substrate serves to minimize any resistance change due to volume expansion of the substrate. Thick film inks usually comprise a conductive filler, e.g. graphite, ruthenium, or silver, in a glass, ceramic, or polymer binder. The binder acts as a matrix for the conductive filler and other components. Those inks in which the binder is a polymer are known as polymer thick film inks (PTF inks).

For some applications, e.g. self-regulating heaters or circuit protection devices, materials exhibiting PTC behavior (positive temperature coefficient of resistance) are preferred. Conductive polymer compositions which exhibit PTC behavior and electrical devices comprising them

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are well-known. Reference may be made, for example, to U.S. Patent Nos. 3,793,716, 3,823,217, 3,858,144, 3,861,029, 3,914,363, 4,017,715, 4,177,376, 4,188,276, 4,237,441, 4,242,573, 4,246,468, 4,286,376, 4,304,987, 4,318,881, 4,330,703, 4,334,148, 4,334,351, 4,388,607, 4,400,614, 4,425,497, 4,426,339, 4,435,639, 4,459,473, 4,514,620, 4,520,417, 4,529,866, 4,534,889, 4,543,474, 4,545,926, 4,547,659, 4,560,498, 4,571,481, 4,574,188, 4,582,983, 4,631,392, 4,638,150, 4,654,511, 4,658,121, 4,659,913, 4,661,687, 4,667,194, 4,673,801, 4,698,583, 4,719,335, 4,722,758, 4,722,853, and 4,761,541, and European Patent Publication Nos. 38,718 (Fouts et al, published October 28, 1981), 158,410 (Batliwalla et al, published October 16, 1985) and 231,068 (Barma et al, published August 5, 1987). The majority of these materials are not suitable for use as inks; rather they are melt-processed or sintered to produce self-supporting articles which have a thickness greater than about 0.002 inch (0.005 cm). The resulting articles may be inflexible and are generally unsuitable for configuration into the intricate or very thin shapes often desirable for use on flexible substrates or printed circuit boards.

U.S. Patent No. 4,722,853 (Batliwalla et al.) discloses a method of applying a PTF ink to a substrate. For these inks, at room temperature the organic polymer binder is in the form of solid particles, i.e. not dissolved, and the solvent is a "latent" solvent, rather than a "true" solvent, for the binder.

U.S. Patent No. 4,628,187 (Sekiguchi et al.) discloses a planar resistive heating element in which a conductive paste is screen-printed between an electrode pattern onto an insulating substrate. The conductive paste, which exhibits

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PTC behavior, comprises a mixture of ethylene/vinyl acetate copolymer, graphite, flame retardant, inert filler, and solvent. A phenolic resin layer deposited over the resistive element provides protection to the element and increases its resistance to thermal degradation when heated to a temperature greater than the melting point of the polymer binder.

SUMMARY OF THE INVENTION

We have now found that polymer thick films with excellent PTC anomalies, good resistance stability under thermal and electrical stress, and good flexibility can be made when the binder comprises a crystalline organic polymer and the solvent is a "true" ("active") solvent for the polymer. Thus, in a first aspect, this invention provides a polymer thick film ink which exhibits PTC behavior and which comprises

- (1) an organic polymer which has a crystallinity of at least 5%;
- (2) an active solvent which is suitable for dissolving the polymer; and
- (3) carbon black which has a pH of less than 4.0.

In a second aspect, this invention comprises an electrical device which comprises an ink of the first aspect.

DETAILED DESCRIPTION OF THE INVENTION

The polymer thick film inks of this invention exhibit PTC (positive temperature coefficient) behavior in the temperature range of interest, i.e. from room temperature

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(defined as 20°C for purposes of this specification) to a temperature comparable to the melting point of the organic polymer of the binder. The melting point, T_m , is defined as the temperature at the peak of the melting curve when the polymer is measured on a differential scanning calorimeter (DSC). The terms "PTC behavior" and "composition exhibiting PTC behavior" are used in this specification to denote a composition which has an R_{14} value of at least 2.5 or an R_{100} value of at least 10, and preferably both, and particularly one which has an R_{30} value of at least 6, where R_{14} is the ratio of the resistivities at the end and the beginning of a 14°C range, R_{100} is the ratio of the resistivities at the end and the beginning of a 100°C range, and R_{30} is the ratio of the resistivities at the end and the beginning of a 30°C range. In contrast, "ZTC behavior" is used to denote a composition which increases in resistivity by less than 6 times, preferably less than 2 times in any 30°C temperature range within the operating range of the heater.

The binder of the thick film ink comprises an organic polymer which has a crystallinity of at least 5%, preferably at least 10%, particularly at least 15%, e.g. 20-30%. Preferred polymers are those which have a crystallinity of less than 60%, particularly less than 50%, especially less than 45%. Polymers with higher crystallinities frequently cannot be dissolved at room temperature. The crystallinity is determined by calculating the heat of fusion as measured by a DSC, and then comparing that value to the 100% crystalline value for a known reference polymer. The choice of polymer for the binder is a function of the desired solvent and the desired switching temperature, where the switching temperature, T_s , is defined as the temperature

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at the intersection point of extensions of the substantially straight portions of a plot of the log of the resistance of a PTC element against temperature which lie on either side of the portion showing the sharp change in slope. T_s is generally slightly less than T_m , although it may be substantially less than T_m depending on the shape of the resistance vs. temperature ($R(T)$) curve. Suitable crystalline polymers include polymers of one or more olefins; copolymers of at least one olefin and at least one monomer copolymerisable therewith, e.g. ethylene/acrylic acid, ethylene/ethyl acrylate, and ethylene/vinyl acetate; polyalkenamers such as polyoctenamer; melt-shapeable fluoropolymers such as polyvinylidene fluoride and copolymers thereof; and blends of two or more such crystalline polymers. The term "fluoropolymer" is used herein to denote a polymer which contains at least 10%, preferably at least 25%, by weight of fluorine, or a mixture of two or more such polymers. Particularly preferred for use in an electrical heater suitable for freeze protection or mirror defrosting is a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene with a melting point of about 88°C, available from Pennwalt under the tradename Kynar 9301.

Suitable solvents are those which are "active" solvents (i.e. "true" solvents) for the polymer binder. Active solvents are defined as those which are capable of interacting with the polymer to produce a mixture throughout which the components are uniformly distributed, in some cases, by dissolving the polymer at room temperature without the application of heat or shear. One skilled in the art will be able to select an appropriate active solvent for a given polymer, either by known solubility data or by experimentation. Dimethyl formamide (DMF) is particularly preferred

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for use with the fluorinated terpolymer (Kynar 9301). Other suitable solvents are isophorone, cyclohexanone and dimethylacetamide. A mixture of solvents may be used when two or more polymers are used in the binder. For these inks each solvent may be a true solvent for each of the polymers, or each solvent may be a true solvent for only one of the polymers. It is preferred that the boiling point of the solvent be greater than the melting point of the polymer binder.

Any carbon black capable of generating a PTC composition may be used. Suitable carbon blacks are disclosed in U.S. Patent Nos. 4,237,441 (van Konynenburg) and 4,388,607 (Toy et al.). Particularly stable inks are produced when the carbon black has a pH of less than 5.0, preferably less than 4.0, particularly less than 3.0, the term "pH of less than 5.0" being used to mean that the pH of the carbon black at the time of mixing with the polymer is less than 5.0. Such blacks may be oxidized. Inks comprising these low pH carbon blacks are useful for heating elements which have relatively high power outputs, i.e. at least 0.5 watt/in², preferably at least 0.75 watt/in², particularly at least 1.0 watt/in², e.g. 1.0 to 2.0 watt/in². The loading of carbon black is a function of the polymer binder, the type and conductivity of the carbon black, and the desired resistivity of the ink for each application. In general, for inks used to form the resistance element of a heater, the weight percent of carbon black is at least 4%, preferably at least 5%, particularly at least 6%. Due to the low shear of the preferred mixing process, lower carbon black loadings may be required for a given resistivity than for traditional blends. A single carbon black may be used, although blends of carbon blacks, or of carbon black and other conductive fillers (e.g. graphite, metals such as

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nickel, or metal oxides) may be used. When a second conductive filler is used in combination with carbon black, the carbon black comprises at least 10%, preferably at least 15%, particularly at least 20%, of the total amount of conductive filler. Inorganic or inert fillers may also be added as, for example, stabilizers, antioxidants, or flow agents.

The components of the ink may be mixed by any method which provides adequate blending, although, unlike conventional inks, the inks of this invention require no kneading or milling. In order to increase the rate at which the polymer binder dissolves, it is preferred that the polymer be in the form of a powder. The polymer powder and the conductive fillers may be mixed together prior to the addition of the solvent, although for some inks, it is preferred that the conductive filler be mixed with the solvent prior to the addition of the polymer. In most cases, the polymer will dissolve in the solvent at room temperature within 24 to 72 hours. The rate of dissolution may be enhanced by gently heating the mixture, although it is important that the solvent remain below its boiling point. The amount of solvent present is dependent on the type of polymer and solvent, the amount of conductive and other filler, and the desired viscosity of the final ink. For screen-printing or other similar application, it is usually preferred that the ink have a viscosity of less than 20,000 cps, e.g. about 7500 to 10,000 cps, preferably 8000 to 9000 cps.

Although the polymer will be completely dissolved in the solvent, the carbon black may settle out of solution. Therefore, prior to use it may be necessary to rapidly mix

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the ink, e.g. by means of a high-speed blender, to generate a uniform mixture. For some applications, the PTC anomaly may be increased by melt-blending the carbon black and other fillers with the polymer prior to dissolving the polymer in the solvent. For these materials, the melt-blended composition may be pelletized, granulated, or otherwise comminuted to produce a powder which can be easily mixed with the solvent.

The ink comprises solids content which is dissolved or distributed in the solvent. The solids content refers to the quantity of polymer and fillers in the ink. Most inks of this invention have a suitable viscosity when the solvent comprises 30 to 80%, preferably 40 to 70%, of the ink by weight.

The substrate may be a rigid material, e.g. alumina or fiberglass, or a flexible material, e.g. a polymer such as polyester, polytetrafluoroethylene, or a conductive polymer. The ink may be applied by screenprinting, spraying, using a doctor blade, or any other suitable technique. It is preferred that the ink be applied in a thickness that will produce a cured layer of at least 0.001 inch (0.0025 cm) thickness. Resistive elements with such a thickness provide increased mechanical strength and higher power density capabilities. In addition, pinholes, which can lead to resistance instability, are minimized.

The ink is cured to evaporate the solvent and solidify the polymer. The term "cure" is used herein to include any solidification of the binder, whether or not it is accompanied by chemical reaction of the binder. In order to maximize the height of the PTC anomaly and ensure binding of

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the ink to the substrate, it is preferred that the temperature of the curing step, T_C , be at least as high as the melting point of the polymer binder, T_m , preferably greater than the melting point of the polymer binder, i.e. T_C is equal to T_m , preferably $(T_m + 10)^\circ\text{C}$, particularly $(T_m + 20)^\circ\text{C}$. The curing step may be accomplished by maintaining the temperature at a constant value or by increasing it stepwise to the desired value. When it is desirable to crosslink the ink, chemical crosslinking may be conducted during the curing process, or the ink may be irradiated after the curing is completed. When T_C is above T_m , curing may be essentially completed in a time of 0.1 to 1.0 hour. Either before or after curing, a dielectric layer may be applied onto the surface of the ink to provide environmental protection and electrical and/or thermal insulation.

The inks are particularly useful in producing the resistive element for an electrical device which is a heater. The ink can be easily applied by means of screen-printing or painting onto a substrate, and can be used to produce complex patterns. The resistivity of the ink and the dimensions of the resistive element can be adjusted when heaters with different resistances, watt densities, or varying thermal requirements are needed. These inks are particularly useful in making the resistive element for heaters. Electrical devices comprising such inks are also useful as circuit protection devices. The pattern produced by the ink may be readily connected to other electronic components, e.g. thick film resistors or varistors, to produce composite devices which have thin cross-sections and rapid thermal transfer.

The invention is illustrated by the following examples.

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Examples 1 - 4

Inks for Examples 1 to 4 were prepared to produce compositions with the solids content listed in Table I. (The final ink formulation included a specific amount of solvent as listed. The weight percent solids in the final composition equaled 100% - % DMF.) The conductive fillers (i.e. carbon black and graphite) were first blended with the solvent and mixed for 5 minutes in a high shear blender. The solution was then filtered through a 120 mesh filter to remove contaminants. Powdered polymer was added to the filtered solution and allowed to stand for 24 to 72 hours. Before printing, the ink was mixed pneumatically for at least 3 minutes to produce a uniform blend with a suitable viscosity (e.g. 8000 to 9000 cps) for printing.

In order to prepare samples of each ink for testing, a silver-based ink (Electrodag[™] 461SS, available from Acheson Colloids) was used to screen-print an interdigitated electrode pattern with 0.25 inch (0.635 cm) spacing between electrodes onto an 0.020 inch thick (0.051 cm) ethylene/tetrafluoroethylene substrate. A layer of PTF ink was applied onto the electrode pattern by means of a doctor blade. The inks were cured by heating in air in a convection oven for 10 minutes at 57°C followed by 15 minutes at 121°C to produce a layer with a thickness of at least 0.001 inch (0.0025 cm). Some samples were irradiated 1 to 6 Mrads.

The resistance vs. temperature characteristics were measured by exposing the samples to five thermal cycles from 21°C to 82°C. The resistivity at 21°C, the height of the PTC anomaly (i.e. the ratio of resistance at 82°C to

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resistance at 21°C), and the thermal stability of the inks, R_n (i.e. the ratio of resistance at 21 degrees on the fifth thermal cycle to that on the first thermal cycle), are reported in Table I. Active powering of the inks at voltages from 60 to 565 VAC for 3 to 24 hours indicated that the inks were stable and displayed a constant current once a steady state condition had been reached.

Table I

Polymer Thick Film Ink Formulations
(Weight Percent of Solids in Total Mix)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
<u>Material</u>					
Kynar™ 9301	82.0	88.0	92.9	87.3	80.0
Raven™ 14	18.0	12.0	7.1	3.9	20.0
Asbury™ M870				8.8	
Weight % DMF	40.0	65.1	40.0	63.8	40.0
Resistivity (ohm-cm)	16	100	1500	530	24
PTC height (82°C)	15	42	410	>1700	171
R_n	1.08	0.96	1.01	0.98	-
Melt process	no	no	no	no	yes

Notes to Table I:

Kynar™ 9301 is a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene with a melting point of about 88°C, available from Pennwalt.

Raven™ 14 is a carbon black with a pH of 3.0 available from Columbian Chemicals.

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Asbury™ M870 is a natural flake graphite with an average particle size of 0.7 microns, available from Asbury Mills.

DMF is dimethyl formamide, a solvent.

Example 5

Using a Brabender™ mixer, 80 wt% powdered Kynar™ 9301 and 20 wt% Raven™ 14 were melt-blended. The mixture was pelletized and was then allowed to dissolve in 40 wt% DMF. The ink was pneumatically mixed, printed, and tested following the procedures of Examples 1 to 4. The results are listed in Table I.

Example 6

Using a resist ink (PR™ 3003, available from Hysol), an electrode pattern was printed onto a substrate comprising 0.0007 inch (0.0018 cm) electrodeposited copper laminated onto 0.005 inch (0.0127 cm) polyester (Electroshield™ C18, available from Lamart). After curing the resist ink in a convection oven, the pattern was etched, leaving copper traces on a polyester backing. The copper traces produced two electrodes, each measuring approximately 0.019 inch (0.048 cm) wide and 200 inches (508 cm) long, which formed a serpentine pattern. The carbon-based ink as described in Example 1 was prepared and screen-printed onto the etched copper polyester laminate in a rectangular pattern approximately 5.5 x 3.5 inch (14.0 x 8.9 cm). After curing the ink, a dielectric layer (Norcote™ 02049, available from Norcote) was screenprinted onto the surface of the ink. Electrical termination was made to the heater by soldering wires onto the copper traces. When powered at 13 VDC, the heater had a power output of approximately 0.7 watts/in² (0.11 w/cm²).

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What is claimed is:

1. A polymer thick film ink which exhibits PTC behavior, said ink comprising

(1) an organic polymer which has a crystallinity of at least 5%;

(2) an active solvent which is suitable for dissolving the polymer; and

(3) carbon black which has a pH of less than 4.0.

2. An ink according to claim 1 wherein the carbon black has a pH of less than 3.0.

3. An ink according to claim 1 or 2 wherein the carbon black has been oxidized.

4. An ink according to claim 1, 2, or 3 wherein the polymer comprises a fluoropolymer.

5. An ink according to any one of the preceding claims wherein the polymer comprises a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene.

6. An ink according to any one of the preceding claims wherein the solvent comprises dimethyl formamide, isophorone, or cyclohexanone.

7. An ink according to any one of the preceding claims which has a viscosity of 7500 to 10,000 cps.

8. An ink according to any one of the preceding claims wherein the polymer has a crystallinity of at least 10%.

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9. An ink according to any one of the preceding claims which further comprises graphite.

10. An electrical device which comprises the polymer thick film ink of any one of the preceding claims and which is a heater or a circuit protection device.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/04011

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 09 D 11/10, H 01 B 1/24																				
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px; vertical-align: top;">IPC5</td> <td style="padding: 5px; vertical-align: top;">C 08 K; C 09 D; H 01 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC5	C 08 K; C 09 D; H 01 B														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US, A, 4491536 (TOMODA ET AL) 1 January 1985, see column 4, line 59 - line 62; column 5, line 5; claims 1-3,10,11</td> <td style="text-align: center; vertical-align: top;">1,4-6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="text-align: center; vertical-align: top;">---</td> <td style="text-align: center; vertical-align: top;">1,4,8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">EP, A2, 0085413 (DAIKIN KOGYO CO., LTD.) 10 August 1983, see page 2, line 23 - line 27; page 6, line 7 - line 18</td> <td style="text-align: center; vertical-align: top;">1,4-7,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US, A, 4482476 (YOSHIMURA ET AL) 13 November 1984, see column 2, line 23 - line 27; column 4, line 23 - line 37; claim 1</td> <td style="text-align: center; vertical-align: top;">1,4-5,9-10</td> </tr> <tr> <td></td> <td style="text-align: center;">---</td> <td></td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4491536 (TOMODA ET AL) 1 January 1985, see column 4, line 59 - line 62; column 5, line 5; claims 1-3,10,11	1,4-6	Y	---	1,4,8	X	EP, A2, 0085413 (DAIKIN KOGYO CO., LTD.) 10 August 1983, see page 2, line 23 - line 27; page 6, line 7 - line 18	1,4-7,9	X	US, A, 4482476 (YOSHIMURA ET AL) 13 November 1984, see column 2, line 23 - line 27; column 4, line 23 - line 37; claim 1	1,4-5,9-10		---	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																				
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: top;"> Date of the Actual Completion of the International Search 11th December 1989 </td> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">0 8. 01. 90</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; vertical-align: top;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: right; font-weight: bold; font-size: 1.2em;">T.K. WILLIS</div> </td> </tr> </table>			Date of the Actual Completion of the International Search 11th December 1989	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">0 8. 01. 90</div>	International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right; font-weight: bold; font-size: 1.2em;">T.K. WILLIS</div>														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	EP, A1, 0235454 (SUNBEAM CORPORATION) 9 September 1987, see page 5, line 5 - line 31; claim 1 --	1,4,8
A	EP, A1, 0068168 (E.I. DU PONT DE NEMOURS AND COMPANY) 5 January 1983, see page 1, line 27 - line 34; abstract; claim 1 --	1-10
A	EP, A1, 0217512 (RAYCHEM CORPORATION) 8 April 1987, see abstract; claims 1-3 -- -----	1-10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 89/04011**

SA 31611

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 08/11/89
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4491536	01/01/85	JP-A- 59059744	05/04/84
		EP-A- 0107793	09/05/84
		JP-A- 59066442	14/04/84
EP-A2- 0085413	10/08/83	JP-A- 58132058	06/08/83
		US-A- 4547311	15/10/85
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		JP-A- 58083066	18/05/83
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		JP-A- 62155502	10/07/87
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